

Theoretical calculation of Gibbs free energy of mixing of biotite: phlogopite-annite-eastonite-siderophyllite system

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ABSTRACT: The Gibbs free energy of mixing (ΔG_{mix}) can be represented as the sum of the ideal mixing energy (ΔG_{id}) and the excess energy (G_{ex}). For biotite in phlogopite (Ph)-annite (An)-eastonite (Es)-siderophyllite (Sd) system, ΔG_{id} is estimated based on MOS (mixing on site) model and G_{ex} is obtained from the theoretically calculated binding energies of biotite. Previous experimental works suggested that Ph-An and possibly Ph-Es pairs form ideal solutions. In this study, however, G_{ex} shows that none of the binary solutions among Ph-An-Es-Sd end-members are ideal. The calculated ΔG_{mix} indicates that Ph-An and Es-Sd pairs form complete solutions, but Ph-Es and An-Sd pairs both mixed by Tschermak's substitution show miscibility gaps. The limit of Tschermak's substitution in biotite is a function of the mole fraction of Fe in the trioctahedral site, $X(\text{Fe})$, and temperature. A comparison of the solvus and spinodal points obtained from the calculated ΔG_{mix} with the chemical compositions of the synthesized and natural biotites implies that Es and Sd are metastable and the limits of Tschermak's substitution are determined not by solvus curves but by spinodal ones. Most chemical compositions of natural biotite fall fairly well within the range defined by the estimated spinodal curves at 800°C, although there are some out-lying biotites especially when their $X(\text{Fe})$ is between 0.5 and 0.7. The general good agreement in limits of Tschermak's substitution between what natural biotite shows and what this study predicts suggests that the theoretical function of thermodynamic mixing of this study seems promising to be applied for understanding the behavior of not only biotite but also other similar solid solutions, particularly when experimental approach is difficult.

Key words: biotite, Gibbs free energy of mixing, ideal mixing energy, excess energy, binding energy, limit of Tschermak's substitution

1. INTRODUCTION

Biotite, an Mg-Fe trioctahedral mica, commonly occurs in various igneous and metamorphic rocks. Natural biotite shows a wide variation in chemical composition due to the great variability in temperature, pressure, and bulk chemical composition of the system in which it forms. The compositional variations in biotite result from cation substitutions among (1) K, Na, and Ca in the interlayer, (2) Li, Mg, Mn, Fe^{2+} , Fe^{3+} , Al, and Ti in the octahedral layer, and (3) Al, Fe^{3+} , and Si in the tetrahedral layer. Attempts have been made to explain these cation substitutions in terms of the stability of biotite as a function of

mixing among end members in various conditions. Among many end members, phlogopite (Ph; $\text{KMg}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$), annite (An; $\text{KFe}^{2+}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$), eastonite (Es; $\text{K}(\text{Mg}_2\text{Al})(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$), and siderophyllite (Sd; $\text{K}(\text{Fe}^{2+}_2\text{Al})(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$) are the main components.

The mixing properties of biotite have been investigated mainly on the binary solutions of Ph-An (Wones, 1963, 1972; Wones and Eugster, 1965; Mueller, 1972), Ph-Es (Crowley and Roy, 1964; Hewitt and Wones, 1975; Robert, 1976; Circone et al., 1991; Circone and Navrotsky, 1992; Yu, 1994), and An-Sd (Rutherford, 1973; Hewitt and Wones, 1975). These studies suggest that Ph-An pair forms an ideal solid solution, but Ph-Es and An-Sd pairs show miscibility gaps of which the compositional ranges are still under debate. The most aluminous synthetic Ph-Es phase was reported as $\text{Ph}_{50}\text{Es}_{50}$ by Crowley and Roy (1964), $\text{Ph}_{38}\text{Es}_{62}$ by Hewitt and Wones (1975), and $\text{Ph}_8\text{Es}_{92}$ by Circone et al. (1991). Rutherford (1973) and Hewitt and Wones (1975) synthesized Fe-Al biotite and proposed that $\text{An}_{25}\text{Sd}_{75}$ is the upper limit of Tschermak's substitution. As can be expected from these experimental results, natural biotite shows almost entire range of Mg-Fe solution. However, the Tschermak's substitution in natural biotite consisting of Ph, An, Es, and Sd components is restricted to less than 0.5 $^{[4]}\text{Al}$ per formula unit based on 12 oxygen atoms (Bailey, 1984; Guidotti, 1984), which is much lower than the Al contents in the synthetic An-Sd of Hewitt and Wones (1975) and Ph-Es of Circone et al. (1991).

Yu (1994) theoretically calculated mixing energy of Ph-Es pair and suggested that the upper limit of Tschermak's substitution could be determined by the spinodal points of the mixing-energy curve rather than by the miscibility gaps. Yu (1994) found that $\text{Ph}_{68}\text{Es}_{32}$ would be the most aluminous phase defined by the miscibility gap at 800°C, but when eastonite was unstable, Ph-Es solution could be more aluminous, up to $\text{Ph}_{47}\text{Es}_{53}$, at the same temperature. The limits of Al content obtained from these theoretical calculations are pertinent to those in natural biotite. Yu (1994) argued that the experimental works could be erroneous in determining the miscibility gaps of biotite because of the difficulties in accurate chemical and

structural analyses and the metastability of the synthetic products. Based on the possible errors in synthesis experiments and the agreement in the limit of Tschermak's substitution between the theoretically calculated and natural phases, Yu (1994) suggested that his approach of mixing-energy calculation can be more helpful in understanding the relationships between the chemical compositions and the stability of Ph-Es solution and could be applied to the other pairs such as Ph-An, An-Sd, and Es-Sd to understand the stability of biotite.

The purpose of this study is to theoretically calculate the mixing energies for Ph-An, An-Sd, and Es-Sd pairs, using the method of Yu (1994) and to elucidate the stability of biotite as a function of chemical composition and temperature in the Ph-Es-An-Sd system. Because none of an ideal An, Es, or Sd phase can be synthesized and, thus, experimental investigations on the mixing property of any pair from these phases are practically impossible, a theoretical approach may be the only way to investigate the stability of these pairs. The method of mixing-energy calculation (Yu, 1994) is fairly straightforward and easy to apply without adopting complicated thermodynamic models. Moreover, the excess energies calculated by the method for Ph-Es pair turned out to be in good agreement with those calorimetrically measured by Circone and Navrotsky (1992). Such agreement persuades that the energy calculation can also be applied to Ph-An, An-Sd, and Es-Sd pairs and interpretation of the results together with those from Yu (1994) should enable to understand the stability of biotite as a function of chemical composition and temperature.

2. METHODS

The procedures of the mixing-energy calculation are described in detail in Yu (1994). The followings are a brief description of the procedures. The Gibbs free energy of mixing, ΔG_{mix} , of a solid-solution phase can be represented as

$$\Delta G_{mix} = \Delta G_{id} + G_{ex}, \quad (1)$$

where ΔG_{id} is the ideal mixing energy and G_{ex} is the excess energy.

ΔG_{id} is the energy accounting for the entropy change caused by random mixing of the components and calculated with "mixing on site (MOS)" model (Nordstrom and Munoz, 1985) as

$$\Delta G_{id} = RT \sum_i X_i \ln a_i^{MOS}, \quad (2)$$

where R is the ideal gas constant, T the absolute temperature, X_i the mole fraction of i th component, and a_i^{MOS} the activity of the i th component calculated on the basis of MOS model. In Ph-An-Es-Sd system, the general

structural chemical formula of biotite can be represented by $K(Al_{X(Al)}Fe^{2+}_{(3-X(Al))X(Fe)})Mg_{(3-X(Al))(1-X(Fe))}(Al_{1+X(Al)}Si_{3-X(Al)})O_{10}(OH)_2$ and then, a_i^{MOS} of the end members become

$$\ln a_{Ph}^{MOS} = \ln \left\{ \left(\frac{(3-X(Al))(1-X(Fe))}{3} \right)^3 \left(\frac{1+X(Al)}{4} \right) \left(\frac{3-X(Al)}{4} \right)^3 \right\} - \ln \left(\frac{27}{256} \right),$$

$$\ln a_{An}^{MOS} = \ln \left\{ \left(\frac{(3-X(Al))X(Fe)}{3} \right)^3 \left(\frac{1+X(Al)}{4} \right) \left(\frac{3-X(Al)}{4} \right)^3 \right\} - \ln \left(\frac{27}{256} \right),$$

$$\ln a_{Es}^{MOS} = \ln \left\{ \left(\frac{(3-X(Al))(1-X(Fe))}{3} \right)^2 \left(\frac{1+X(Al)}{4} \right) \left(\frac{1+X(Al)}{4} \right)^2 \left(\frac{3-X(Al)}{4} \right)^2 \right\} - \ln \left(\frac{4}{432} \right),$$

and

$$\ln a_{Sd}^{MOS} = \ln \left\{ \left(\frac{(3-X(Al))X(Fe)}{3} \right)^2 \left(\frac{X(Al)}{3} \right) \left(\frac{1+X(Al)}{4} \right)^2 \left(\frac{3-X(Al)}{4} \right)^2 \right\} - \ln \left(\frac{4}{432} \right).$$

G_{ex} is the energy accounting for any deviation from ideality of mixing and resolved into excess enthalpy H_{ex} and excess entropy S_{ex} terms:

$$G_{ex} = H_{ex} - TS_{ex}. \quad (3)$$

If the constituent cations of biotite are randomly mixed, $S_{ex}=0$ and Equation 3 becomes

$$G_{ex} = H_{ex}. \quad (4)$$

The excess enthalpy can be calculated from the binding energy of mixing, E_{mix} , defined by

$$E_{mix} = E_{ss} - E_{mech} = E_{ss} - \sum_i X_i E_i, \quad (5)$$

where E_{ss} and E_i are the calculated binding energies of a solid-solution phase and the i th end member forming the solution phase. The binding energies are calculated with the Ewald method (Ewald, 1921) on a partly ionic model (Yu, 1990, 1994). Comparing the calculated binding energies with the enthalpies of formation for phlogopite and annite from Helgeson et al. (1978) gives the following relation:

$$G_{ex} = H_{ex} = (0.4087(1-X(Fe)) + 0.3668X(Fe)) E_{mix}. \quad (6)$$

The Gibbs free energy of mixing can be obtained by

substituting Equations 2 and 6 into Equation 1.

3. RESULTS AND DISCUSSION

Examining the mixing properties of the binary solutions of two end members may be the first step to understand the whole mixing properties of biotite in Ph-An-Es-Sd system. Table 1 summarizes calculated E_{ss} , E_{mix} ,

G_{ex} , and $\ln a_i^{MOS}$ of biotite along Ph-An, Ph-Es, An-Sd, and Es-Sd joins. Figures 1 and 2 show G_{ex} and ΔG_{mix} , respectively, as a function of the mole fraction of respective end members of each binary solution. Figure 1 suggests that none of the binary solutions are ideal in contrary to the data suggested by Wones and Eugster (1965) and Circone et al. (1991). The mixing behavior of each binary pair is described in detail in the following.

Table 1. Calculated binding energies of the solutions (E_{ss}), binding energies of mixing between the end members (E_{mix}), and excess energies (G_{ex}) calculated from E_{mix} , with the activities of the end-members of the solutions along Ph-An, Ph-Es, An-Sd, and Es-Sd joins. All the energies are in kcal/mole.

| $X(Fe)$ | $X(Al)$ | E_{cal} | E_{mix} | G_{ex} | $\ln a_1$ | $\ln a_2$ |
|-------------------|---------|-----------|-----------|----------|-----------|-----------|
| <i>Ph-An pair</i> | | | | | <i>Ph</i> | <i>An</i> |
| 0.0 | 0.0 | -3642.576 | 0.000 | 0.000 | 0.000 | — |
| 0.1 | 0.0 | -3614.317 | -0.038 | -0.015 | -0.316 | -6.908 |
| 0.2 | 0.0 | -3586.314 | -0.332 | -0.133 | -0.669 | -4.828 |
| 0.3 | 0.0 | -3558.581 | -0.895 | -0.355 | -1.070 | -3.612 |
| 0.4 | 0.0 | -3531.067 | -1.678 | -0.658 | -1.532 | -2.749 |
| 0.5 | 0.0 | -3503.792 | -2.700 | -1.047 | -2.079 | -2.079 |
| 0.6 | 0.0 | -3475.296 | -2.501 | -0.959 | -2.749 | -1.532 |
| 0.7 | 0.0 | -3445.953 | -1.455 | -0.552 | -3.612 | -1.070 |
| 0.8 | 0.0 | -3416.904 | -0.702 | -0.264 | -4.828 | -0.669 |
| 0.9 | 0.0 | -3388.119 | -0.214 | -0.079 | -6.908 | -0.316 |
| 1.0 | 0.0 | -3359.608 | 0.000 | 0.000 | — | 0.000 |
| <i>Ph-Es pair</i> | | | | | <i>Ph</i> | <i>Es</i> |
| 0.0 | 0.0 | -3642.576 | 0.000 | 0.000 | 0.000 | — |
| 0.0 | 0.1 | -3688.158 | 0.775 | 0.317 | -0.108 | -2.012 |
| 0.0 | 0.2 | -3733.876 | 1.414 | 0.578 | -0.232 | -1.285 |
| 0.0 | 0.3 | -3779.776 | 1.870 | 0.764 | -0.370 | -0.865 |
| 0.0 | 0.4 | -3825.892 | 2.111 | 0.863 | -0.522 | -0.580 |
| 0.0 | 0.5 | -3872.134 | 2.226 | 0.910 | -0.688 | -0.376 |
| 0.0 | 0.6 | -3918.583 | 2.134 | 0.872 | -0.869 | -0.228 |
| 0.0 | 0.7 | -3965.170 | 1.904 | 0.778 | -1.064 | -0.123 |
| 0.0 | 0.8 | -4011.994 | 1.436 | 0.587 | -1.273 | -0.053 |
| 0.0 | 0.9 | -4058.977 | 0.810 | 0.331 | -1.498 | -0.013 |
| 0.0 | 1.0 | -4106.144 | 0.000 | 0.000 | — | 0.000 |
| <i>An-Sd pair</i> | | | | | <i>An</i> | <i>Sd</i> |
| 0.0 | 0.0 | -3359.608 | 0.000 | 0.000 | 0.000 | — |
| 0.0 | 0.1 | -3414.999 | -1.785 | -0.655 | -0.108 | -2.012 |
| 0.0 | 0.2 | -3470.825 | -4.004 | -1.469 | -0.232 | -1.285 |
| 0.0 | 0.3 | -3524.282 | -3.855 | -1.414 | -0.370 | -0.865 |
| 0.0 | 0.4 | -3576.052 | -2.019 | -0.740 | -0.522 | -0.580 |
| 0.0 | 0.5 | -3628.234 | -0.594 | -0.218 | -0.688 | -0.376 |
| 0.0 | 0.6 | -3680.818 | 0.428 | 0.157 | -0.869 | -0.228 |
| 0.0 | 0.7 | -3733.855 | 0.997 | 0.366 | -1.064 | -0.123 |
| 0.0 | 0.8 | -3787.320 | 1.138 | 0.418 | -1.273 | -0.053 |
| 0.0 | 0.9 | -3841.297 | 0.768 | 0.282 | -1.498 | -0.013 |
| 0.0 | 1.0 | -3895.671 | 0.000 | 0.000 | — | 0.000 |
| <i>Es-Sd pair</i> | | | | | <i>Es</i> | <i>Sd</i> |
| 0.0 | 0.0 | -4106.144 | 0.000 | 0.000 | 0.000 | — |
| 0.1 | 0.0 | -4084.529 | 0.568 | 0.230 | -0.211 | -4.605 |
| 0.2 | 0.0 | -4063.047 | 1.002 | 0.401 | -0.446 | -3.219 |
| 0.3 | 0.0 | -4041.677 | 0.325 | 0.525 | -0.713 | -2.408 |
| 0.4 | 0.0 | -4020.473 | 1.482 | 0.581 | -1.022 | -1.833 |
| 0.5 | 0.0 | -3999.331 | 1.576 | 0.611 | -1.386 | -1.386 |
| 0.6 | 0.0 | -3978.374 | 1.486 | 0.570 | -1.833 | -1.022 |
| 0.7 | 0.0 | -3957.522 | 1.291 | 0.490 | -2.408 | -0.713 |
| 0.8 | 0.0 | -3936.760 | 1.006 | 0.377 | -3.219 | -0.446 |
| 0.9 | 0.0 | -3916.157 | 0.561 | 0.208 | -4.605 | -0.211 |
| 1.0 | 0.0 | -3895.671 | 0.000 | 0.000 | — | 0.000 |

3.1. Ph-An Mixing

Figure 1a shows that G_{ex} on Ph-An join has negative values, which is very rare for an excess energy. The excess energies do not fit to the commonly accepted Margules equation of Thompson (1967) with the terms up to the third order of the mole fraction (X). Exact fitting of the excess energy in Figure 1a to the generalized Margules equation requires the terms of more than 7th order of X , which is not only practically meaningless but also seriously problematic in interpreting the mixing behavior (Navrotsky, 1987). ΔG_{mix} curves in Figure 2a are all concave downward and Ph-An pair, thus, should have no miscibility gap, forming a complete solid solution.

Previous studies (Wones, 1972; Mueller, 1972) suggested that Ph-An pair forms an ideal solution. This study, however, indicates that the mixing of the pair is complete, but not ideal.

3.2. Ph-Es Mixing

The G_{ex} values in Figure 1b are adopted from Yu (1994) who used the Margules parameters of $W_{Ph}=9.089$ and $W_{Es}=8.737$ kcal/mole to represent G_{ex} in the form of Margules equation: $G_{ex}=X(Al)(1-X(Al))[W_{Ph}X(Al) + W_{Es}(1-X(Al))]$. The ΔG_{mix} values from Yu (1994; Fig. 2b) indicate that Ph-Es pair has miscibility gaps when temperature is below 1200°C. Figure 3a shows the solvus and spinodal points obtained from the ΔG_{mix} curves in Figure 2b. The solvus and spinodal points satisfy the following equations:

$$\frac{dG_{mix}}{dX}(1-X) + G_{mix} = 0 \quad (7)$$

$$\text{and } \frac{d^2 G_{mix}}{dX^2} = 0, \quad (8)$$

respectively. The solutions of Equations 7 and 8 are ob-

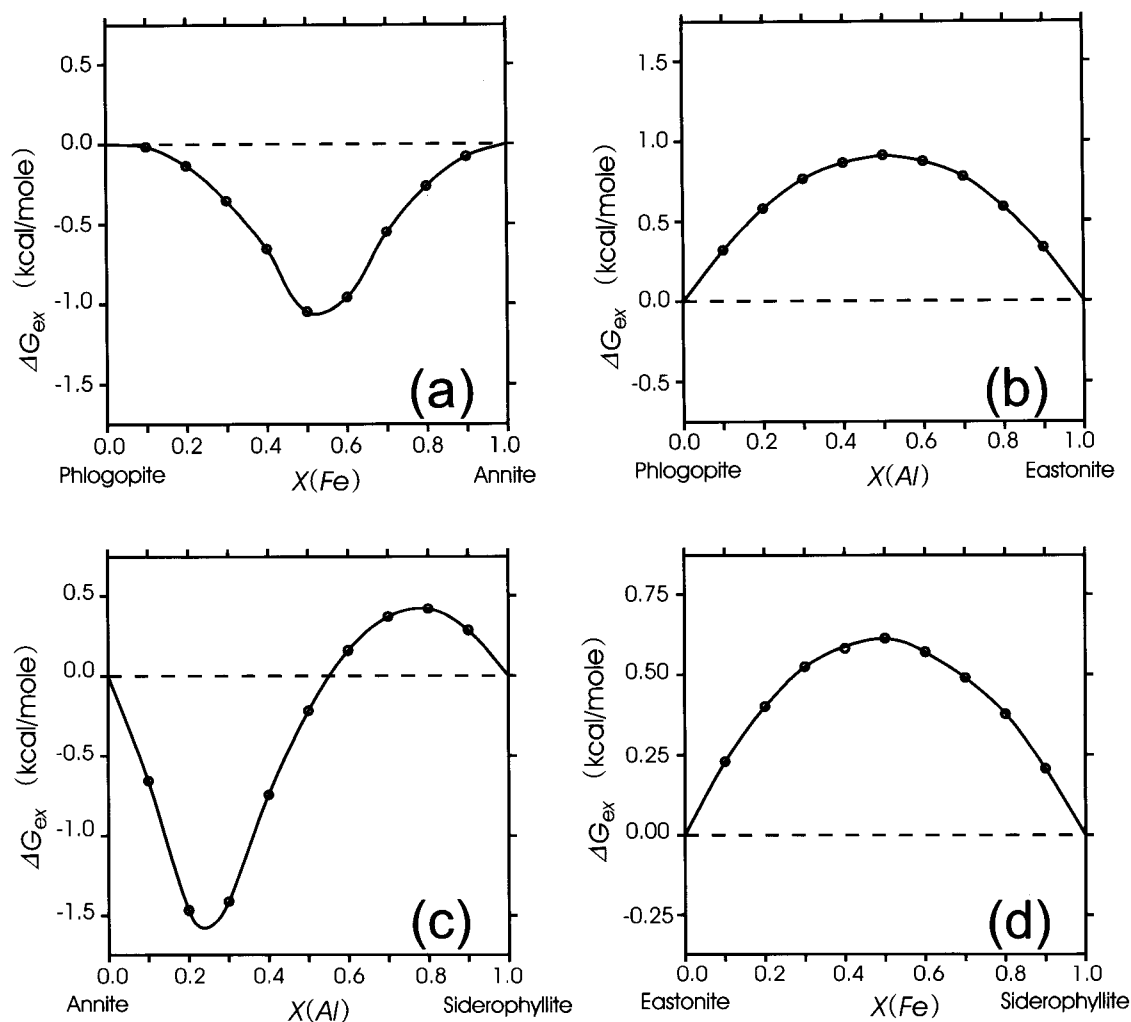


Fig. 1. G_{ex} calculated from the binding energies for the binary solutions along (a) Ph-An, (b) Ph-Es, (c) An-Sd, and (d) Es-Sd joins.

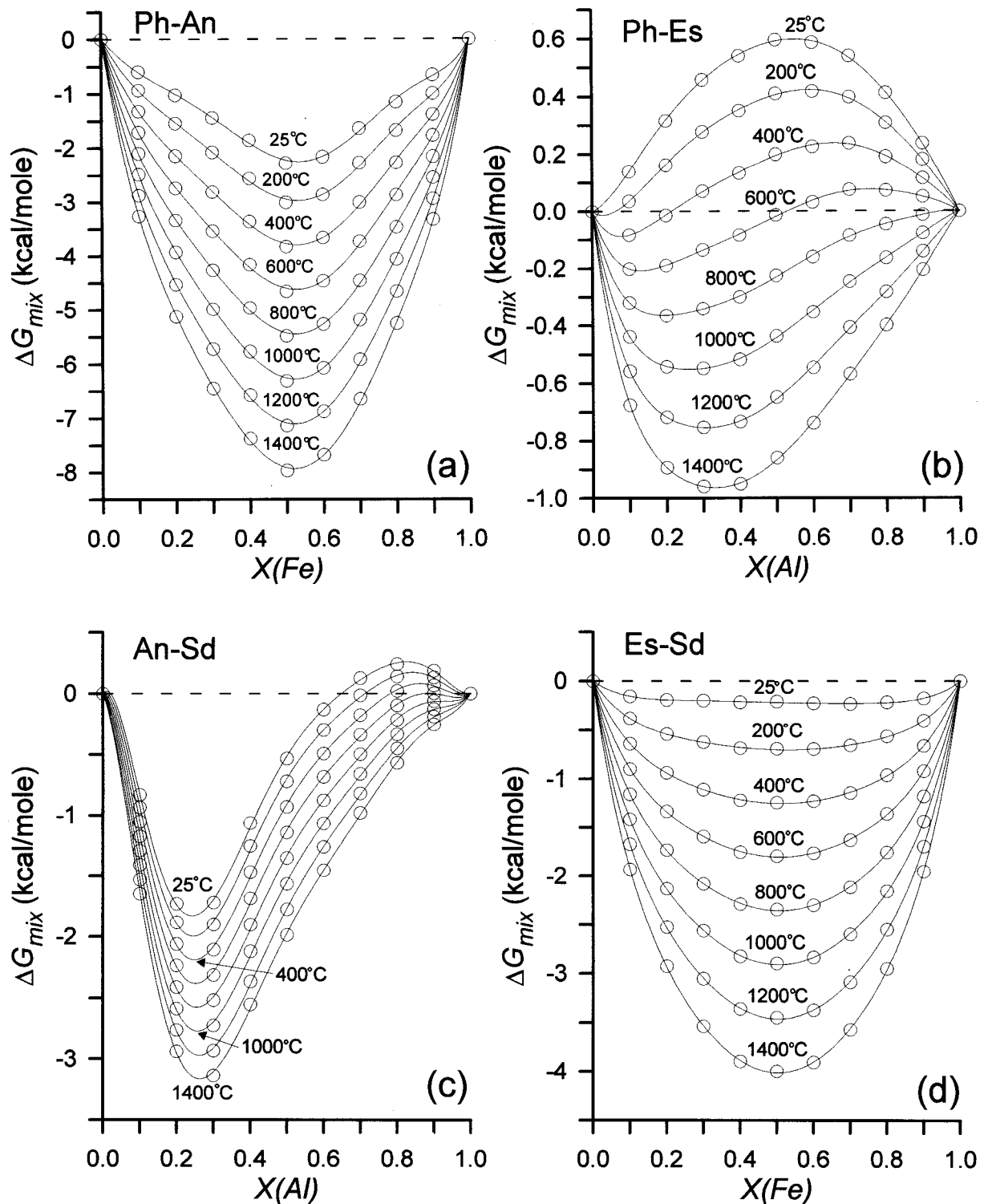


Fig. 2. ΔG_{mix} curves at different temperatures for the binary solutions along (a) Ph-An, (b) Ph-Es, (c) An-Sd, and (d) Es-Sd joins.

tained with the Newton-Raphson method of approximation (Luenberger, 1989).

The upper limits of Tschermak's substitution defined by the solvus curve in Figure 3a, which is $\text{Ph}_{0.35}\text{Es}_{0.65}$ at

800°C, are in good agreement with those found among natural biotites (Guidotti, 1984). However, these limits are much lower than those of synthesized Ph-Es solutions. This may reflect that it is the spinodal points that

determine the upper limits of Tschermak's substitution, since Es is unstable (Yu, 1994). The most aluminous composition defined by the spinodal curve in Figure 3a is 0.55 at 800°C, which is fairly close to what Crowley and Roy (1964) and Hewitt and Wones (1975) reported. Circone et al. (1991) reported $\text{Ph}_8\text{Es}_{92}$ as the most aluminous phase but their results seem to be erroneous (Yu, 1994).

3.3. An-Sd Mixing

As in the case of Ph-An pair, G_{ex} of An-Sd pair in Figure 1c does not fit to the conventional Margules equation. ΔG_{mix} in Figure 2c indicates that An-Sd pair also has miscibility gaps. Figure 3b shows the calculated solvus and spinodal points from the ΔG_{mix} curves in Figure 2c with the Newton-Raphson method.

It has been relatively well known that An-Sd pair shows nonideal mixing behavior. However, the upper limits of Tschermak's substitution defined either by the solvus curve ($X(\text{Al})=0.30$ at 800°C) or by the spinodal curve ($X(\text{Al})=0.41$ at 800°C) (Fig. 3b) are much lower than what Rutherford (1973) and Hewitt and Wones (1975) reported ($X(\text{Al})=0.75$ at 700–850°C). This disagreement in the upper limits of $X(\text{Al})$ between the theoretical calculations and the experimental syntheses may be caused by the metastability of Sd as in the case of Ph-Es mixing. In natural biotites, pure An-Sd solutions are rarely found, because most geological systems have Mg with Fe and a Fe-octahedral layer is more unstable than an Mg-octahedral layer owing to its greater size misfitting to the tetrahedral layer. Although pure Fe-Al biotite is hardly found, there are many natural ferrous biotites having $X(\text{Fe}) > 0.7$ which are fairly correspondent to the An-Sd solutions. The maximum $X(\text{Al})$ of these natural ferrous biotites is less than 0.4, which is very close to the limit of Tschermak's substitution defined by the spinodal curve in Figure 3b. It suggests that the synthesized high-aluminous An-Sd solutions and consequently, Sd are metastable. Thus, the limits of Tschermak's substitution along An-Sd join may be actually controlled by spinodal curves rather than solvus ones. There are some natural ferryannites having much higher $X(\text{Al})$ than 0.4. These high-aluminous ferryannites, however, commonly have considerable amounts of either tetrahedral Fe^{3+} or octahedral vacancies to fit the octahedral layer into the size of the tetrahedral layer (Dyar and Burns, 1986). These high-aluminous ferryannites are out of the scope of this study.

3.4. Es-Sd Mixing

Figure 1d shows the calculated G_{ex} values for Es-Sd pair. The Margules parameters for $G_{\text{ex}}=X(\text{Fe})(1-X(\text{Fe}))$

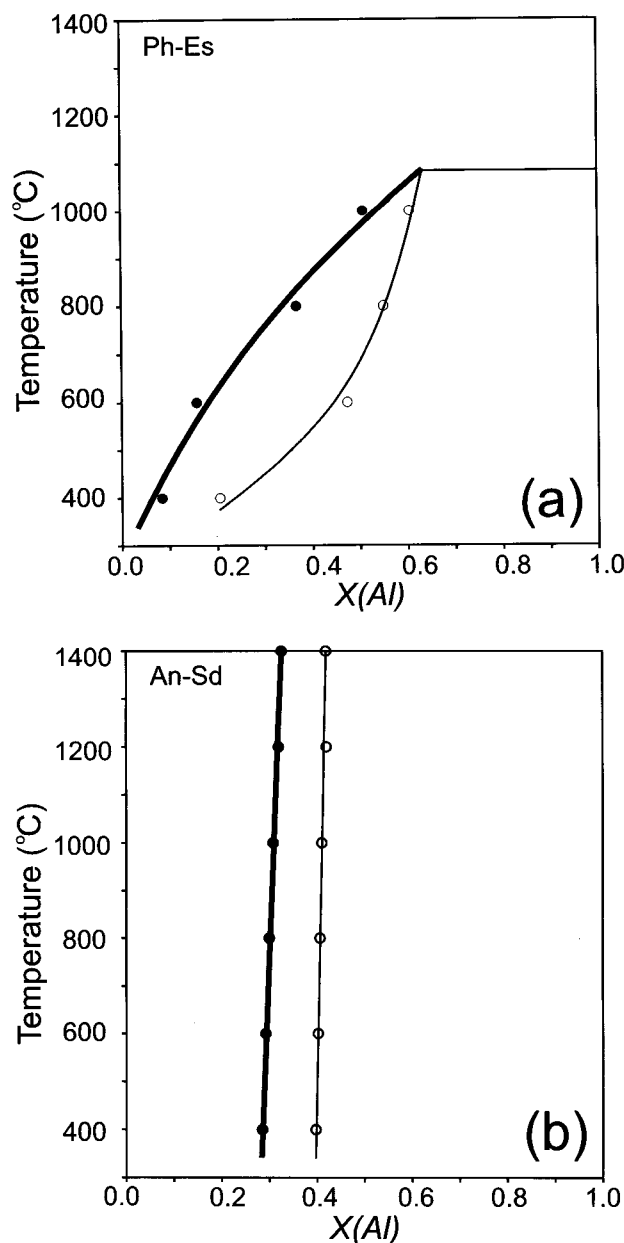


Fig. 3. Solvus curves (thick curves connecting the solid circles) and spinodal curves (thin curves connecting the open circles) obtained from ΔG_{mix} curves in Figure 2 for (a) Ph-Es and (b) An-Sd pairs.

$[W_{\text{Es}}X(\text{Fe})+W_{\text{Sd}}(1-X(\text{Fe}))]$ are $W_{\text{Es}}=2.257$ and $W_{\text{Sd}}=2.572$ kcal/mole. The Es-Sd pair may have miscibility gaps at relatively lower temperatures because of the positive G_{ex} , but the miscibility gap quickly disappears as temperature increases, resulting in a complete solid solution as ΔG_{mix} indicates (Fig. 2d).

Because neither Es nor Sd has been successfully synthesized or reported to occur in any natural systems, no investigation on the mixing properties of Es-Sd pair has been made. Thus, the calculated mixing properties

can not be compared with those suggested by experimental results nor by the chemical compositions of natural biotites.

3.5. Ph-An-Es-Sd Mixing

The mixing properties of the two end-member pairs discussed above suggest that biotite has miscibility gaps only in Tschermak's substitution. Fe-Mg exchange shows no miscibility gap for both of Ph-An and Es-Sd pairs. Thus, the mixing behavior of biotite in Ph-An-Es-Sd system should be described in terms of mixing between two solid solutions, Ph-An and Es-Sd, having the same $X(Fe)$. For example, a biotite having the composition of $Ph_{0.35}An_{0.35}Es_{0.15}Sd_{0.15}$ ($K(Al_{0.3}Fe_{1.35}Mg_{1.35})(Al_{1.3}Si_{2.7})O_{10}(OH)_2$) should be considered as a result of mixing between $An_{50}Ph_{50}$ ($K(Fe_{1.5}Mg_{1.5})(AlSi_3)O_{10}(OH)_2$) and $Es_{50}Sd_{50}$ ($K(Al_{1.0}Fe_{1.0}Mg_{1.0})(Al_2Si_2)O_{10}(OH)_2$) with a ratio of 7:3.

Table 2 lists E_{ss} , E_{mix} , and G_{ex} of biotite in Ph-An-Es-Sd system, calculated on the basis of binary mixing between the Ph-An and the Es-Sd solutions having the same $X(Fe)$. a_i^{MOS} for each end-member of the solutions is calculated in the same way as those for Ph-Es solutions. With these energies and activities, ΔG_{mix} curves for a constant $X(Fe)$ are obtained, and solvus and spinodal points are estimated from the ΔG_{mix} curves using the Newton-Raphson method. Figure 4 shows an example of the calculated ΔG_{mix} curves for a $Ph_{50}An_{50}$ - $Es_{50}Sd_{50}$ pair.

Figure 5 represents how the calculated solvus and spinodal points vary according to the temperature, $X(Fe)$, and $X(Al)$. If both Es and Sd are unstable as discussed earlier, the limit of Tschermak's substitution should be defined not by the solvus points but by the spinodal points. Figure 6 compares the tetrahedral Al contents of natural biotite with the calculated limits of Tschermak's substitution at different temperatures. The calculated limit of Tschermak's substitution at 800°C embraces all the Al contents of natural biotites all over the ranges of $X(Fe)$ except $0.5 < X(Fe) < 0.7$. It suggests that the theoretically calculated thermodynamic functions in this study for mixing of biotite in Ph-An-Es-Sd system highly possibly control the limit of chemical composition of natural biotite when $X(Fe)$ is greater than 0.7 or lower than 0.5.

The presence of some natural biotites more aluminous than the calculated limits of Tschermak's substitution may be attributed to the possible errors in estimation of thermodynamic mixing functions or the influence of the other chemical components, excluded in this study, on the stability of biotite. ΔG_{mix} curves around $X(Fe)=0.7$ show significant uncertainties due to the considerable scattering of the calculated values. Thus, the estimated solvus and spinodal points from these curves may not be correct and can be shifted to more aluminous direction up to $X(Al)=0.5$. Although the spinodal points around $X(Fe)=$

Table 2. Calculated binding energies (E_{ss}) of the solutions, binding energies of mixing (E_{mix}), and excess energies (G_{ex}) for biotite in Ph-An-Es-Sd system. All the energies are in kcal/mole.

| $X(Fe)$ | $X(Al)$ | E_{ss} | E_{mix} | G_{ex} |
|---------|---------|-----------|-----------|----------|
| 0.1 | 0.0 | -3614.317 | 0.000 | 0.000 |
| 0.1 | 0.1 | -3660.458 | 0.880 | 0.356 |
| 0.1 | 0.2 | -3706.788 | 1.571 | 0.636 |
| 0.1 | 0.3 | -3752.905 | 2.476 | 1.001 |
| 0.1 | 0.4 | -3799.998 | 2.404 | 0.972 |
| 0.1 | 0.5 | -3846.904 | 2.519 | 1.019 |
| 0.1 | 0.6 | -3894.012 | 2.432 | 0.984 |
| 0.1 | 0.7 | -3941.305 | 2.160 | 0.874 |
| 0.1 | 0.8 | -3988.841 | 1.646 | 0.666 |
| 0.1 | 0.9 | -4036.565 | 0.943 | 0.381 |
| 0.1 | 1.0 | -4084.529 | 0.000 | 0.000 |
| 0.3 | 0.0 | -3558.581 | 0.000 | 0.000 |
| 0.3 | 0.1 | -3605.796 | 1.095 | 0.434 |
| 0.3 | 0.2 | -3653.244 | 1.956 | 0.775 |
| 0.3 | 0.3 | -3700.895 | 2.615 | 1.036 |
| 0.3 | 0.4 | -3748.823 | 2.996 | 1.187 |
| 0.3 | 0.5 | -3796.996 | 3.133 | 1.241 |
| 0.3 | 0.6 | -3845.386 | 3.053 | 1.209 |
| 0.3 | 0.7 | -3894.083 | 2.665 | 1.056 |
| 0.3 | 0.8 | -3942.988 | 2.070 | 0.820 |
| 0.3 | 0.9 | -3992.224 | 1.143 | 0.453 |
| 0.3 | 1.0 | -4041.677 | 0.000 | 0.000 |
| 0.5 | 0.0 | -3503.792 | 0.000 | 0.000 |
| 0.5 | 0.1 | -3552.083 | 1.263 | 0.490 |
| 0.5 | 0.2 | -3600.601 | 2.299 | 0.891 |
| 0.5 | 0.3 | -3649.402 | 3.052 | 1.183 |
| 0.5 | 0.4 | -3698.478 | 3.530 | 1.369 |
| 0.5 | 0.5 | -3747.826 | 3.735 | 1.448 |
| 0.5 | 0.6 | -3797.506 | 3.609 | 1.400 |
| 0.5 | 0.7 | -3847.503 | 3.166 | 1.228 |
| 0.5 | 0.8 | -3897.770 | 2.453 | 0.951 |
| 0.5 | 0.9 | -3948.399 | 1.378 | 0.534 |
| 0.5 | 1.0 | -3999.331 | 0.000 | 0.000 |
| 0.7 | 0.0 | -3445.953 | 0.000 | 0.000 |
| 0.7 | 0.1 | -3499.252 | -2.142 | -0.182 |
| 0.7 | 0.2 | -3548.860 | -0.593 | -0.225 |
| 0.7 | 0.3 | -3598.714 | 0.710 | 0.269 |
| 0.7 | 0.4 | -3648.902 | 1.679 | 0.637 |
| 0.7 | 0.5 | -3699.416 | 2.322 | 0.881 |
| 0.7 | 0.6 | -3750.314 | 2.580 | 0.979 |
| 0.7 | 0.7 | -3801.527 | 2.524 | 0.958 |
| 0.7 | 0.8 | -3853.157 | 2.051 | 0.778 |
| 0.7 | 0.9 | -3905.132 | 1.233 | 0.468 |
| 0.7 | 1.0 | -3957.522 | 0.00 | 0.000 |
| 0.9 | 0.0 | -3388.119 | 0.000 | 0.000 |
| 0.9 | 0.1 | -3442.752 | -1.829 | -0.670 |
| 0.9 | 0.2 | -3497.946 | -4.219 | -1.565 |
| 0.9 | 0.3 | -3548.902 | -2.372 | -0.880 |
| 0.9 | 0.4 | -3600.154 | -0.820 | -0.304 |
| 0.9 | 0.5 | -3651.771 | 0.367 | 0.136 |
| 0.9 | 0.6 | -3703.810 | 1.132 | 0.420 |
| 0.9 | 0.7 | -3756.242 | 1.504 | 0.558 |
| 0.9 | 0.8 | -3809.144 | 1.405 | 0.521 |
| 0.9 | 0.9 | -3862.411 | 0.942 | 0.350 |
| 0.9 | 1.0 | -3916.157 | 0.000 | 0.000 |

0.7 may be considerably underestimated, it alone can not explain all the biotite with chemical compositions outside

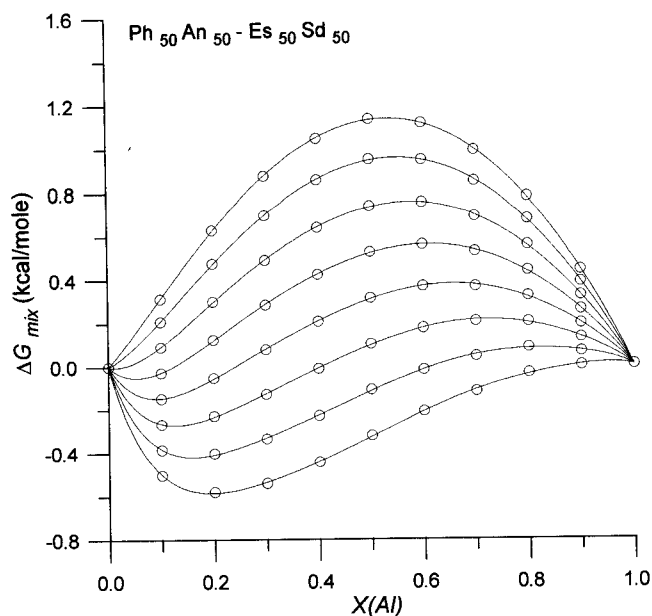


Fig. 4. ΔG_{mix} curves at different temperatures for the binary solutions of $Ph_{50}An_{50}-Es_{50}Sd_{50}$ pair.

the estimated range. The main reason is rather attributable to the effects of the other components not incorporated in this study, such as Ca^{2+} and Na^{+} at the interlayer cation site, Li^{+} , Mn^{2+} , Fe^{3+} , Ti^{4+} , and vacancies at the octahedral cation site, Fe^{3+} at the tetrahedral cation site, and F^{-} and Cl^{-} at the octahedral OH^{-} site of biotite. All or some of these components always exist in natural biotite in various amounts and affect the stability of biotite. Especially,

biotite tends to have more Fe^{3+} in the tetrahedral cation site or more vacancies in the octahedral cation site as the amount of octahedral Fe^{2+} increases. Future research on the theoretical calculation of the Gibbs free energy of mixing should include the chemical components which are not considered in this study.

4. SUMMARY

The theoretical calculation of the Gibbs free energy of mixing (ΔG_{mix}) of biotite suggests that none of the pairs among Ph, An, Es, and Sd form ideal solutions. Ph-An and Es-Sd pairs, however, can form complete solid solutions, whereas binary solutions of Ph-Es or An-Sd pair have miscibility gaps. Margules parameters of the calculated excess energies (G_{ex}) for Ph-Es and Es-Sd pairs are estimated to be $W_{Ph}=9.087$ and $W_{Es}=8.737$, and $W_{Es}=2.257$ and $W_{Sd}=2.572$, respectively. Because of the instability of eastonite and siderophyllite, the upper limits of Tschermak's substitution of aluminous biotite probably depend on the chemical composition defined not by solvus points but by the spinodal points of ΔG_{mix} .

The upper limits of Tschermak's substitution defined by the spinodal points, which occur at $X(Al)=0.55$ on the Ph-Es join and at $X(Al)=0.41$ on the An-Sd join, fairly well confine the compositions of natural biotites except some biotites having $0.5 < X(Fe) < 0.7$. The agreement in the compositional ranges predicted by this study with those of the natural biotites indicates that theoretical calculation of the mixing energies is very helpful in

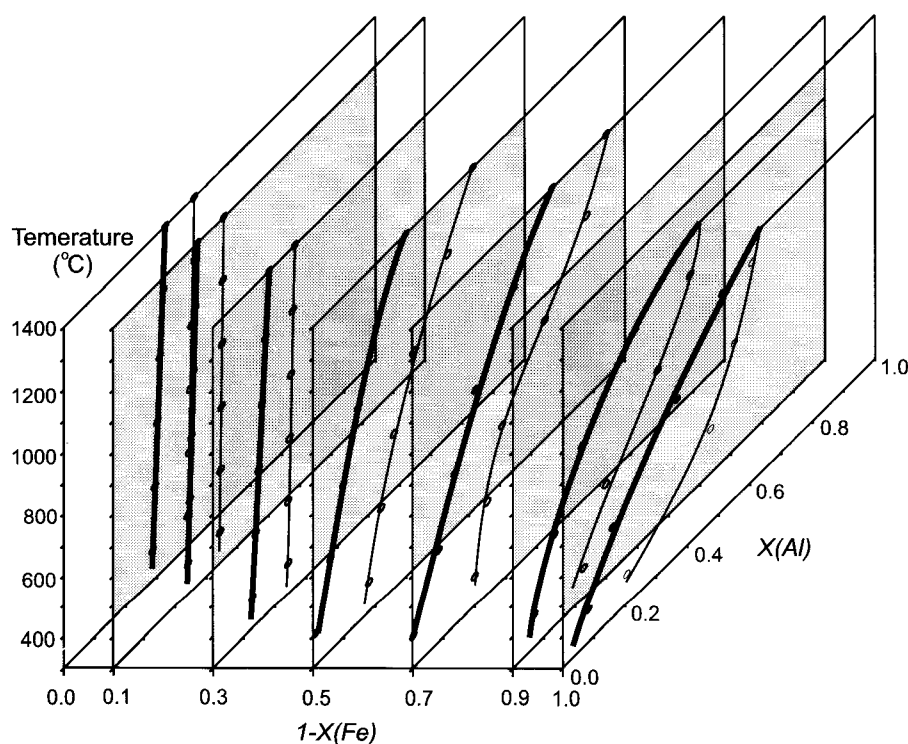


Fig. 5. The solvus and spinodal curves as a function of temperature and $X(Fe)$ for biotite in Ph-An-Es-Sd system.

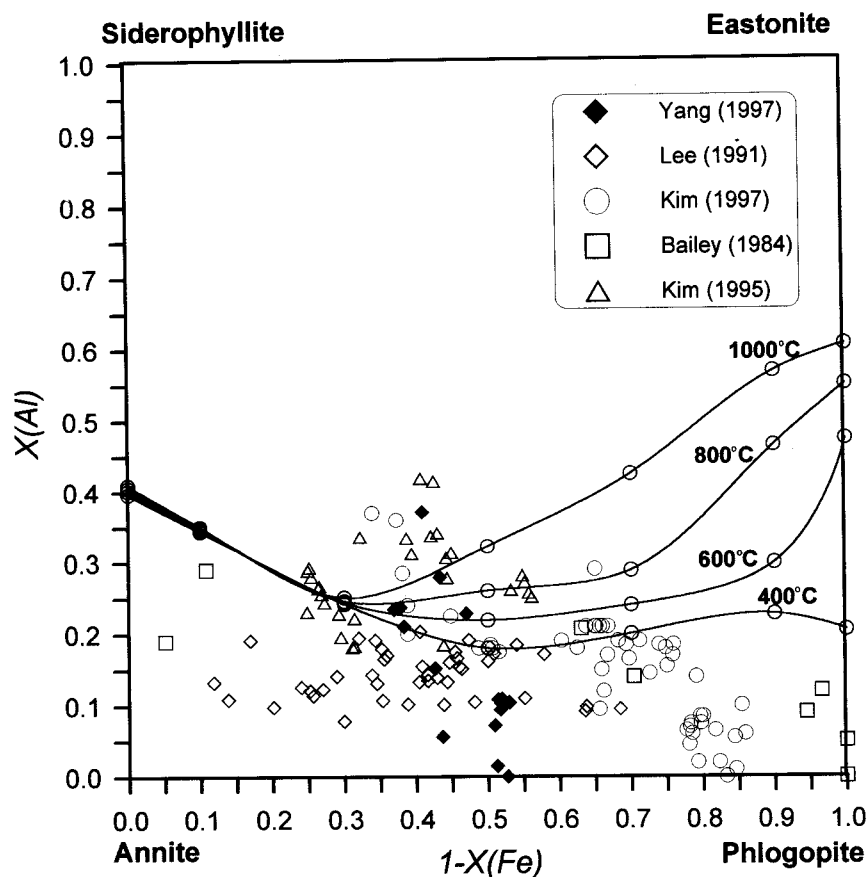


Fig. 6. Comparison of the limits of Tschermak's substitution curves estimated from the spinodal curves in Figure 5 with the chemical compositions of natural biotites from Bailey (1984, open squares), Lee (1991, open diamonds), Kim (1995, open triangles), Kim (1997, open circles), and Yang (1997, solid diamonds).

understanding the relationship between the chemical composition and the stability of biotite in greater detail, which is essential to correctly decipher the geological processes imposed on the interested terrain. A theoretical estimation of thermodynamic functions can be similarly utilized for other solid solutions, particularly when there are difficulties in experimental investigation on thermodynamic mixing properties of the solid solutions.

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